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(54) PRODUCTION OF FUNCTIONAL CARBONACEOUS MATERIAL

(57)Abstract:
PROBLEM TO BE SOLVED: To form carbon nanotube, hollow onion-like carbon or metal-including onion-like carbon in high purity and yield, furthermore to directly form a thin film therefrom on a substrate.
SOLUTION: This functional carbonaceous material is obtained according to the following process: polytetrafluoroethylene, polyvinylidene chloride or polyvinylidene fluoride is exposed to an arc discharge atmosphere to form the objective amorphous carbon including at least one kind among carbon nanotube, hollow onion-like carbon and onion-like carbon, wherein it is preferable that the atmospheric gas to be used in the arc discharge is helium at 760-300 Torr.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the following remarkable effects are attained.
(1) Since a carbon nanotube, hollow-onion-like carbon, metal-endocyst-hollow-onion-like carbon, etc. are made to form in the front face, using resin films, such as poly tetrafluoro carbon, a polyvinylidene chloride, and a polyvinylidene fluoride, as a raw material, refining separation of a product is easy.
(2) Since a functional carbon material is formed in the above-mentioned resin film front face, these functional thin films can be formed on a substrate.
(3) The carbon nanotube thin film obtained by this appearance demonstrates the electronic physical properties and chemical property which are predicted theoretically.
(4) The obtained carbon nanotube thin film is useful also as abrasion resistance material, the emitter for electron ray discharge, the high directivity radiation source, the source of a soft X ray, single dimension conduction material, high temperature conduction material, other electronic material, etc.

PRIOR ART

[Description of the Prior Art] Carbon nanotube (it may only be called a "nanotube" below), It is compounded under existence of a catalyst metal by gaseous-phase methods, such as a carbon arc process, a sputtering technique, and the laser beam irradiating method, by using carbon materials, such as amorphous carbon or graphite, as a raw material (references, such as JP,6-157016,A, JP,6-280116,A, JP,6-227806,A, JP,6-283129,A, JP,6-322615,A, JP,6-325623,A, JP,7-197325,A, JP,7-165406,A, JP,8-188406,A, and JP,9-31757,A). However, by this method, since graphites other than a nanotube, amorphous carbon, etc. were intermingled in the product, mixing of not only a low but the catalyst metal to the inside of a nanotube was not avoided for yield. Moreover, in order that it might be intermingled in the generated soot and a nanotube might generate, it was difficult to form a thin film in the shape of a substrate.

TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the manufacturing method of functional carbon materials, such as a carbon nanotube, hollow-onion-like carbon, and metal-endocyst-onion-like carbon. In addition, in this invention, a core is hollow and "hollow-onion-like carbon" means the carbon particle of the shape of the spherical from which the graphite laminated structure has developed into the circumference in the shape of an onion, or a polyhedron. In such hollow-onion-like carbon, the laminating of the graphite layer is carried out to ten layers of numbers from several layers. Moreover, "the hollow-onion-like carbon which connotes a metal" means the carbon particle of the shape of the spherical to which metal particles exist in the hollow of the core of the above-mentioned "hollow-onion-like carbon", or a polyhedron. Although especially the metal to connote is not limited, Mg, aluminum, Au, etc. are illustrated, for example.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[The technical field to which invention belongs] this invention relates to the manufacturing method of functional carbon materials, such as a carbon nanotube, hollow-onion-like carbon, and metal-endocyst-onion-like carbon. In addition, in this invention, a core is hollow and "hollow-onion-like carbon" means the carbon particle of the shape of the spherical from which the graphite laminated structure has developed into the circumference in the shape of an onion, or a polyhedron. In such hollow-onion-like carbon, the laminating of the graphite layer is carried out to ten layers of numbers from several layers. Moreover, "the hollow-onion-like carbon which connotes a metal" means the carbon particle of the shape of the spherical to which metal particles exist in the hollow of the core of the above-mentioned "hollow-onion-like carbon", or a polyhedron. Although especially the metal to connote is not limited, Mg, aluminum, Au, etc. are illustrated, for example.
[Description of the Prior Art] Carbon nanotube (it may only be called a "nanotube" below), It is compounded under existence of a catalyst metal by gaseous-phase methods, such as a carbon arc process, a sputtering technique, and the laser beam irradiating method, by using carbon materials, such as amorphous carbon or graphite, as a raw material (references, such as JP,6-157016,A, JP,6-280116,A, JP,6-227806,A, JP,6-283129,A, JP,6-322615,A, JP,6-325623,A, JP,7-197325,A, JP,7-165406,A, JP,8-188406,A, and JP,9-31757,A). However, by this method, since graphites other than a nanotube, amorphous carbon, etc. were intermingled in the product, yield is not only low, but mixing of the catalyst metal to the inside of a nanotube was not avoided. Moreover, in order that it might be intermingled in the generated soot and a nanotube might generate, it was difficult to form a thin film in the shape of a substrate.
[Problem(s) to be Solved by the Invention] Therefore, this invention sets it as the main purposes to form a carbon nanotube, hollow-onion-like carbon, or metal-endocyst-onion-like carbon by high yield and the high grade. Furthermore, this invention aims also at forming these thin films directly on a substrate.
[Means for Solving the Problem] As a result of advancing research in view of the present condition of the above technology, this invention person uses a polytetrafluoroethylene, a polyvinylidene chloride, or a polyvinylidene fluoride as a raw material, and came to complete the technology which forms a carbon nanotube, hollow-onion-like carbon, metal-endocyst-onion-like carbon, or such inclusion by exposing these raw materials to arc discharge. That is, this invention is; which is what offers the manufacturing method of the functional carbon material shown below.
1. a polytetrafluoroethylene, a polyvinylidene chloride, or a polyvinylidene fluoride -- arc discharge atmosphere -- **** -- the manufacturing method of the functional carbon material characterized by generating the amorphous carbon containing at least one sort of a carbon nanotube, hollow-onion-like carbon, and metal-endocyst-onion-like carbon by things
2. Manufacturing method of a functional carbon material given in the above-mentioned term 1 using the helium of 760 - 300torr as a controlled atmosphere at the time of arc discharge.
[Embodiments of the Invention] Manufacture of functional carbon materials, such as a

carbon nanotube by the conventional arc discharge method By generating a carbon arc in gaseous helium by using carbon material, such as amorphous carbon and graphite, as an electrode, and making it deposit on a cathode surface it has been carried out (above-mentioned JP,6-157016,A and JP,6-280116,A --) JP,6-227806,A, JP,6-283129,A, JP,6-322615,A, Refer to JP,6-325623,A, JP,7-197325,A, JP,7-165406,A, JP,8-188406,A, JP,9-31757,A, etc. For example, if the gap between carbon electrodes is kept at about 1mm and stable arc discharge is made to maintain, the sediment of the shape of a pillar with the almost same diameter as the diameter of an anode bar will be formed at the nose of cam of cathode. An arc current grows for the diameter of 6mm, in 70A (voltage is 25V), a sediment grows [an anode plate carbon rod] with the speed of about 2-3mm per minute, and the maximum yield is obtained when helium is about 500 torr(s). Subsequently, the method of distributing the sediment to the nose of cam of cathode to ethanol using an ultrasonic wave etc., and separating by the filter, column separation, etc. is common. Therefore, formation of a functional carbon-material thin film is impossible. on the other hand, direct [by exposing film-like a polytetrafluoroethylene (PTFE), a polyvinylidene chloride, or a polyvinylidene fluoride to arc discharge / in a resin film] in this invention -- carbon ---izing -- a carbon nanotube, hollow-onion-like carbon, or metal-endocyst-onion-like carbon -- the inclusion of these is made to form In this method, since these functional carbon materials were formed in a resin film front face, the separation refining became easy as compared with the conventional technology, and thin film-ization was attained. Arc discharge to the resin film in this invention is performed using electrodes, such as a tungsten in gaseous helium atmosphere of about 760-300 torrs of pressures, and molybdenum, and impressing the direct current voltage of 10-50V. Subsequently, it is among solvents, such as ethanol, a tetrahydrofuran, and diethylether, for example, the film black-ized by electric discharge is cleaned ultrasonically, by-products, such as soot, are removed, and a desired functional carbon material is obtained. Since forming polyyne structure by reduction is known when using PTFE as a resin, a polyyne is formed in the interior of a film front face and/or a film of arc discharge, and it is guessed that this is that in which functional carbon materials, such as a carbon nanotube, are formed. Metal-endocyst-onion-like carbon is formed when metal particles exist in the interior of a resin film, and/or a front face. That is, to the resin film containing metal particles, by performing arc discharge by the same technique as the above, metal particles are incorporated by the centrum of onion-like carbon, and metal-endocyst-onion-like carbon is formed. Grant of the metal particles to a resin film can be performed by the method of plating a metal on a resin film front face with well-known resin plating technology, or kneading a metal particle (10 micrometers or less) beforehand in a resin raw material at the time of film manufacture. Furthermore, by heating the above-mentioned metal-endocyst-onion-like carbon under reduced pressure, hollow-onion-like carbon can fuse a metal and can manufacture it by making it evaporate and remove.

[Effect of the Invention] According to this invention, the following remarkable effects are attained.

(1) Since a carbon nanotube, hollow-onion-like carbon, metal-endocyst-hollow-onion-like carbon, etc. are made to form in the front face, using resin films, such as poly tetrafluoro carbon, a polyvinylidene chloride, and a polyvinylidene fluoride, as a raw material, refining separation of a product is easy.

(2) Since a functional carbon material is formed in the above-mentioned resin film front

face, these functional thin films can be formed on a substrate.
(3) The carbon nanotube thin film obtained by this appearance demonstrates the electronic physical properties and chemical property which are predicted theoretically.
(4) The obtained carbon nanotube thin film is useful also as abrasion resistance material, the emitter for electron ray discharge, the high directivity radiation source, the source of a soft X ray, single dimension conduction material, high temperature conduction material, other electronic material, etc.
[Example] The cylinder-like PTFE film with a diameter [example 1 / of 20mm] and a length of 20mm was made, and the wolfram electrode (diameter of 10mm) was put in from the ends of the open end, respectively, and it adjusted so that two inter-electrode distance might be set to 3mm. Under the present circumstances, it was made for a cylinder-like film and an electrode not to contact. In such the state, after installing a cylinder-like PTFE film and two electrodes into the vacuum chamber and decompressing to 10-4torr with a rotary pump and a molecule turbine pump, argon gas was introduced and the inside of a chamber was set to 500torr(s). Subsequently, DC arc electric discharge (voltage 25V) was carried out by inter-electrode [two], and the PTFE film was carbonized. The change of current was about 90A of a certain thing. It will be in the state where a film burns in several minutes and a hole opens, after discharge starting. After having collected these films, cleaning ultrasonically in ethanol and removing soot-like carbon, the film was observed with the transmission electron microscope. Thereby, it was checked that a multilayer carbon nanotube and hollow-onion-like carbon are generating on the PTFE film front face. PTFE is carbonized by arc discharge and this is considered that a nanotube and onion-like carbon were formed by heating a carbonization object further. On the occasion of composition of a nanotube etc., it is already pointed out that it may pass through a polyyne as the intermediate field. Since it is known that PTFE will make polyyne structure by reduction, also in this example, a polyyne is first formed into a film front face and/or a film of arc discharge, and this is considered to have changed to a nanotube and onion-like carbon further.
The cylinder-like polyvinylidene chloride film with a diameter [example 2 / of 20mm] and a length of 20mm was made, and arc discharge processing was carried out like the example 1. Subsequently, after cleaning the film which carbonized ultrasonically in ethanol, when it observed with the transmission electron microscope, a carbon nanotube and onion-like carbon were observed. It is known that a polyvinylidene chloride will take polyyne structure by reduction like PTFE. Also in this example, this polyyne serves as intermediate field and it is thought that it changed to a nanotube and onion-like carbon.
The cylinder-like polyvinylidene-fluoride film with a diameter [example 3 / of 20mm] and a length of 20mm was made, and arc discharge processing was carried out like the example 1. Subsequently, after cleaning the film which carbonized ultrasonically in ethanol, when it observed with the transmission electron microscope, a carbon nanotube and onion-like carbon were observed. It is known that a polyvinylidene chloride will take polyyne structure by reduction like PTFE. Also in this example, this polyyne serves as intermediate field and it is thought that it changed to a nanotube and onion-like carbon.
The PTFE film with a thickness of 30 micrometers was installed with the hotpress to the stainless steel plate with an example 4 thickness of 0.3mm. This is cast with a bore [of 20mm], and a length of 20mm in the shape of a cylinder, a wolfram electrode (diameter of 10mm) is put in from the ends of the open end, respectively, and it was made for two

inter-electrode distance to be set to 3mm. Under the present circumstances, it was made for the cylinder and electrode which make PTFE a inner layer not to contact. In this state, a cylinder-like PTFE film and two electrodes were installed into the vacuum chamber, and carried out arc discharge for 3 minutes like the example 1, ethanol washing was carried out, and it observed with the transmission electron microscope. It was checked that the functional carbon thin film to which amorphous carbon and a carbon nanotube exist in a stainless steel plate internal surface simultaneously is formed.
Five PTFE films (30mmx100mmx30micrometer) were prepared into example 5 ferric-chloride solution (0.1 mol/l), hydrazine solution (0.1 mol/l) was mixed, and both the front faces of a film were plated with iron. Arc discharge was presented with the obtained iron plating PTFE film like the example 1, and subsequently, after carrying out ethanol washing, it observed with the transmission electron microscope. Consequently, much hollow-onion-like carbon which connotes an iron particle was observed. It turns out that this invention method is effective as one of the processes of metal-particles-endocyst-hollow-onion-like carbon.
Five PTFE films (30mmx100mmx30micrometer) were taught to example 6 magnesium-chloride solution (0.1 mol/l), hydrazine solution (0.1 mol/l) was mixed, and both the front faces of a film were plated with magnesium. After presenting arc discharge with the obtained magnesium plating PTFE film like an example 5, it observed with the transmission electron microscope. In here, much hollow-onion-like carbon which connotes a magnesium particle was observed. Subsequently, when the temperature up of the sample electrode holder of an electron microscope was carried out to 800degreeC, the magnesium particle evaporated, and was removed and formation of hollow-onion-like carbon was observed. Therefore, it turns out that this invention method is effective as a process of hollow-onion-like carbon.

CLAIMS

[Claim(s)]
[Claim 1] a polytetrafluoroethylene, a polyvinylidene chloride, or a polyvinylidene fluoride -- arc discharge atmosphere -- **** -- the manufacturing method of the functional carbon material characterized by generating the amorphous carbon containing a carbon nanotube, hollow-onion-like carbon, metal-endocyst-onion-like carbon, or these at least one sort by things
[Claim 2] The manufacturing method of the functional carbon material according to claim 1 using the helium of 760 - 300torr as a controlled atmosphere at the time of arc discharge.